

THE CLAIMSWHAT IS CLAIMED IS:

- 5 *sk* 1. A semiconductor wafer cleaning formulation, comprising the following components in the percentage by weight ranges shown, based on the total weight of such components:

	fluoride source	1-21%
5	organic amine(s)	
	20-55%	
	a nitrogenous component, selected from nitrogen-containing	
	carboxylic acids and imines	0.5-40%
	water	23-50%
10	<u>metal chelating agent(s)</u>	<u>0-21%</u>
	TOTAL	100%

- 15 2. The cleaning formulation of claim 1 wherein said fluoride source comprises a fluoride species selected from the group consisting of:

ammonium fluoride; and
triethanolammonium fluoride (TEAF).

3. The cleaning formulation of claim 1 wherein said organic amine(s) comprise an amine selected from the group consisting of:

diglycolamine (DGA),
methyldiethanolamine (MDEA),

pentamethyldiethylenetriamine (PMDETA),
triethanolamine (TEA), and
triethylenediamine (TEDA).

4. The cleaning formulation of claim 1 wherein said nitrogenous component comprises a species selected from the group consisting of:

iminodiacetic acid (IDA);
glycine;
nitrilotriacetic acid (NTA); and
1,1,3,3-tetramethylguanidine (TMG).

5. The cleaning formulation of claim 1 including at least one metal chelating agent selected from the group consisting of:

acetoacetamide,
ammonium carbamate,
ammonium pyrrolidinedithiocarbamate (APDC),
dimethyl malonate,
methyl acetoacetate,
N-methyl acetoacetamide,
2,4-pentanedione,
tetramethylammonium thiobenzoate,
tetramethylammonium trifluoroacetate, and
tetramethylthiuram disulfide (TMTDS).

6. The cleaning formulation of claim 1 wherein said fluoride source comprises a species selected from the group consisting of:

ammonium fluoride,
triethanolammonium fluoride (TEAF),
5 diglycolammonium fluoride (DGAF),
tetramethylammonium fluoride (TMAF), and
triethylamine tris (hydrogen fluoride) (TREAT-HF).

7. The cleaning formulation of claim 1 wherein said organic amine(s) comprises an amine selected from the group consisting of:

10 diglycolamine (DGA),
methyldiethanolamine (MDEA),
pentamethyldiethylenetriamine (PMDETA),
triethanolamine (TEA),
triethylenediamine (TEDA),
15 hexamethylenetetramine,
3, 3-iminobis (N,N-dimethylpropylamine), and
monoethanolamine.

8. The cleaning formulation of claim 1, wherein said nitrogenous component comprises a species from the group consisting of:

iminodiacetic acid (IDA)
glycine
nitrilotriacetic acid (NTA)

1,1,3,3-tetramethylguanidine (TMG)

$\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$

$\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$

$\text{CH}_3\text{C}(=\text{NH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$

$(\text{CH}_3\text{CH}_2)_2\text{NC}(=\text{NH})\text{N}(\text{CH}_3\text{CH}_2)_2$

$\text{HOOCCH}_2\text{N}(\text{CH}_3)_2$

$\text{HOOCCH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$

9. The cleaning formulation of claim 1 wherein said fluoride source comprises a species selected from the group consisting of:

Ammonium fluoride,

triethanolammonium fluoride (TEAF),

diglycolammonium fluoride (DGAF),

tetramethylammonium fluoride (TMAF), and

triethylamine tris (hydrogen fluoride) (TREAT-HF);

said organic amine(s) comprise a species selected from the group consisting of:

diglycolamine (DGA),

methyldiethanolamine (MDEA),

pentamethyldiethylenetriamine (PMDETA),

triethanolamine (TEA),

triethylenediamine (TEDA),

hexamethylenetetramine,

3, 3'-iminobis (N,N-dimethylpropylamine), and

monoethanolamine;

said nitrogenous component comprises a species selected from the group consisting of:

iminodiacetic acid (IDA)

glycine

nitrilotriacetic acid (NTA)

1,1,3,3-tetramethylguanidine (TMG)

and said formulation includes a metal chelating agent comprising a species selected from the group consisting of:

acetoacetamide,

ammonium carbamate,

5 ammonium pyrrolidinedithiocarbamate (APDC),

dimethyl malonate,

methyl acetoacetate,

N-methyl acetoacetamide,

2,4-pentanedione,

10 tetramethylammonium thiobenzoate,

tetramethylammonium trifluoroacetate, and

tetramethylthiuram disulfide (TMTDS).

10. The cleaning formulation of claim 1 wherein said fluoride source comprises a compound having the general formula $R_1R_2R_3R_4NF$ in which each of the R groups is independently selected from hydrogen atoms and aliphatic groups, and wherein said formulation includes a metal chelating agent of the formula:

X-CHR-Y, in which

R is either hydrogen or an aliphatic group and

20 X and Y are functional groups containing multiply bonded moieties having electron-withdrawing properties.

11. The cleaning formulation of claim 10 wherein each of X and Y is independently selected from CONH₂, CONHR', CN, NO₂, SOR', and SO₂Z in which R' is alkyl and Z is hydrogen, halo, or alkyl.

12. The cleaning formulation of claim 1 wherein said fluoride source comprises a compound having the formula R₁R₂R₃R₄NF in which each of the R groups is hydrogen or aliphatic, and wherein said
5 formulation includes a metal chelating agent of the formula, R₁R₂R₃R₄N⁺O₂CCF₃ in which each of the R groups is independently hydrogen or aliphatic.

13. The cleaning formulation of claim 1, wherein said nitrogenous component includes a compound having the formula:

10 COOH-CH₂-NRR'

wherein each of R and R' is independently selected from the group consisting of hydrogen, alkyl, aryl, and carboxylic acids.

14. A method for fabricating a semiconductor wafer, comprising:

plasma etching a metalized layer from a surface of the wafer;

15 plasma ashing a resist from the surface of the wafer;

cleaning the wafer by contacting same with a cleaning formulation, comprising the following components in the percentage by weight ranges shown, based on the total weight of such components:

20	fluoride source	1-21%
	organic amine(s)	20-55%
	a nitrogenous component, selected from nitrogen-containing carboxylic acids and imines	0.5-40%

water	23-50%
metal chelating agent(s)	0-21%
TOTAL	100%

5 15. The method of claim 14 wherein said fluoride source comprises a fluoride species selected from the group consisting of:

ammonium fluoride; and
triethanolammonium fluoride (TEAF).

10 16. The method of claim 14 wherein said organic amine(s) comprise an amine selected from the group consisting of:

diglycolamine (DGA),
methyldiethanolamine (MDEA),
pentamethyldiethylenetriamine (PMDETA),
triethanolamine (TEA), and
15 triethylenediamine (TEDA)

17. The method of claim 14 wherein said nitrogenous component comprises a species selected from the group consisting of:

iminodiacetic acid (IDA);
glycine;
nitrilotriacetic acid (NTA); and
1,1,3,3-tetramethylguanidine (TMG).

18. The method of claim 14 including at least one metal chelating agent selected from the group consisting of:

acetoacetamide,
ammonium carbamate,
5 ammonium pyrrolidinedithiocarbamate (APDC),
dimethyl malonate,
methyl acetoacetate,
N-methyl acetoacetamide,
2,4-pentanedione,
10 tetramethylammonium thiobenzoate,
tetramethylammonium trifluoroacetate, and
tetramethylthiuram disulfide (TMTDS).

19. The method of claim 14 wherein said fluoride source comprises a species selected from the group consisting of:

15 ammonium fluoride,
triethanolammonium fluoride (TEAF)
diglycolammonium fluoride (DGAF),
tetramethylammonium fluoride (TMAF) and
triethylamine tris (hydrogen fluoride) (TREAT-HF).

20 20. The method of claim 14 wherein said organic amine(s) comprises an amine selected from the group consisting of:

diglycolamine (DGA),
methyldiethanolamine (MDEA),

pentamethyldiethylenetriamine (PMDETA),
 triethanolamine (TEA),
 triethylenediamine (TEDA),
 hexamethylenetetramine,
 5 3, 3-iminobis (N,N-dimethylpropylamine), and
 monoethanolamine.

21. The method of claim 14, wherein said nitrogenous component comprises a species from the group consisting of:

iminodiacetic acid (IDA)
 glycine
 nitrilotriacetic acid (NTA)
 1,1,3,-tetramethylguanidine (TMG)
 $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$
 $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$
 $\text{CH}_3\text{C}(=\text{NH})\text{CH}_2\text{C}(\text{O})\text{CH}_3$
 $(\text{CH}_3\text{CH}_2)_2\text{NC}(=\text{NH})\text{N}(\text{CH}_3\text{CH}_2)_2$
 $\text{HOOCCH}_2\text{N}(\text{CH}_3)_2$
 $\text{HOOCCH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$

22. The method of claim 14 wherein said fluoride source comprises a species selected from the group consisting of:

10 ammonium fluoride,
 triethanolammonium fluoride (TEAF),

diglycolammonium fluoride (DGAF),
 tetramethylammonium fluoride (TMAF), and
 triethylamine tris (hydrogen fluoride) (TREAT-HF);

said organic amine(s) comprise a species selected from the group consisting of:

- 5 diglycolamine (DGA),
 methyldiethanolamine (MDEA),
 pentamethyldiethylenetriamine (PMDETA),
 triethanolamine (TEA),
 triethylenediamine (TEDA),
 10 hexamethylenetetramine,
 3, 3-iminobis (N,N-dimethylpropylamine), and
 monoethanolamine;

said nitrogenous component comprises a species selected from the group consisting of:

iminodiacetic acid (IDA)
 glycine
 nitrilotriacetic acid (NTA)
 1,1,3,3-tetramethylguanidine (TMG)

and said formulation includes a metal chelating agent comprising a species selected from the group consisting of:

- 15 acetoacetamide,
 ammonium carbamate,
 ammonium pyrrolidinedithiocarbamate (APDC),
 dimethyl malonate,
 methyl acetoacetate,
 20 N-methyl acetoacetamide,

2,4-pentanedione,

tetramethylammonium thiobenzoate,

tetramethylammonium trifluoroacetate, and

tetramethylthiuram disulfide (TMTDS).

- 5 23. The method of claim 14 wherein said fluoride source comprises a compound having the general formula $R_1R_2R_3R_4NF$ in which each of the R groups is independently selected from hydrogen atoms and aliphatic groups, and wherein said formulation includes a metal chelating agent of the formula:

X-CHR-Y, in which

- 10 R is either hydrogen or an aliphatic group and

X and Y are functional groups containing multiply bonded moieties having electron-withdrawing properties.

- 15 24. The method of claim 23 wherein each of X and Y is independently selected from $CONH_2$, $CONHR'$, CN , NO_2 , SOR' , and SO_2Z in which R' is alkyl and Z is hydrogen, halo, or alkyl.

25. The method of claim 14 wherein said fluoride source comprises a compound having the formula $R_1R_2R_3R_4NF$ in which each of the R groups is hydrogen or aliphatic, and wherein said formulation includes a metal chelating agent of the formula, $R_1R_2R_3R_4N^+O_2CCF_3$ in which each of the R groups is independently hydrogen or aliphatic.

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26. The method of claim 14, wherein said nitrogenous component includes a compound having the formula:

$COOH-CH_2-NRR'$

wherein each of R and R' is independently selected from the group consisting of hydrogen, alkyl, aryl, and carboxylic acids.

27. A method for fabricating a semiconductor wafer including the steps comprising:

5 plasma etching a metalized layer from a surface of the wafer;

plasma ashing a resist from the surface of the wafer;

cleaning the wafer by contacting same with a cleaning formulation, comprising the following components in the percentage by weight ranges shown, based on the total weight of such components:

10	a fluoride source;	1-21%
	at least one organic amine;	20-55%
	a nitrogen-containing carboxylic acid or imine	0.5-40%
	water;	23-50%
	<u>at least one metal chelating agent</u>	<u>0-21%</u>
15	TOTAL	100%

28. The method of claim 27 wherein said fluoride source is chosen from the group consisting of:

ammonium fluoride; and

triethanolammonium fluoride (TEAF).

20 29. The method of claim 27 wherein said organic amine is chose from the group consisting of:

diglycolamine (DGA),

methyldiethanolamine (MDEA),

pentamethyldiethylenetriamine (PMDETA),

triethanolamine (TEA), and

triethylenediamine (TEDA).

30. The method of claim 27 wherein said nitrogen-containing carboxylic acid or imine is selected from the group consisting of:

iminodiacetic acid (IDA)

glycine

nitrilotriacetic acid (NTA)

1,1,3,3-tetramethylguanidine (TMG)

31. The method of claim 27 wherein said metal chelating agent is selected from the group consisting of:

acetoacetamide,

ammonium carbamate,

ammonium pyrrolidinedithiocarbamate (APDC),

dimethyl malonate,

methyl acetoacetate,

N-methyl acetoacetamide,

2,4-pentanedione,

tetramethylammonium thiobenzoate,

tetramethylammonium trifluoroacetate, and

tetramethylthiuram disulfide (TMTDS).

32. The method of claim 27 wherein said fluoride source is selected from the group consisting of:

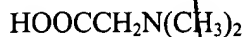
ammonium fluoride,
triethanolammonium fluoride (TEAF),
diglycolammonium fluoride (DGAF),
tetramethylammonium fluoride (TMAF), and
5 triethylamine tris (hydrogen fluoride) (TREAT-HF).

33. The method of claim 27 wherein said organic amine is selected from the group consisting of:

diglycolamine (DGA),
methyldiethanolamine (MDEA),
pentamethyldiethylenetriamine (PMDETA),
10 triethanolamine (TEA),
triethylenediamine (TEDA),
hexamethylenetetramine,
3, 3-iminobis (N,N-dimethylpropylamine), and
monoethanolamine.

15 34. The method of claim 27, wherein said nitrogen-containing carboxyl acid or imine is selected from the group consisting of:

iminodiacetic acid (IDA)
glycine
nitrilotriacetic acid (NTA)
1,1,3,-tetramethylguanidine (TMG)
 $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$
 $\text{CH}_3\text{C}(=\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH})\text{CH}_2\text{C}(\text{O})\text{N}(\text{CH}_3)_2$



35. The method of claim 27 wherein said fluoride source is selected from the group consisting of:

ammonium fluoride,

triethanolammonium fluoride (TEAF),

5 diglycolammonium fluoride (DGAF),

tetramethylammonium fluoride (TMAF), and

triethylamine tris (hydrogen fluoride) (TREAT-HF);

said organic amine is chosen from the group consisting of:

diglycolamine (DGA),

10 methyldiethanolamine (MDEA),

pentamethyldiethylenetriamine (PMDETA),

triethanolamine (TEA),

triethylenediamine (TEDA),

hexamethylenetetramine,

15 3, 3-iminobis (N,N-dimethylpropylamine), and

monoethanolamine;

said nitrogen-containing carboxylic acid or imine is chosen from the group consisting of:

iminodiacetic acid (IDA)

glycine

nitrilotriacetic acid (NTA)

1,1,3,3-tetramethylguanidine (TMG)

and said metal chelating agent is selected from the group consisting of:

acetoacetamide,
 ammonium carbamate,
 ammonium pyrrolidinedithiocarbamate (APDC),
 5 dimethyl malonate,
 methyl acetoacetate,
 N-methyl acetoacetamide,
 2,4-pentanedione,
 tetramethylammonium thiobenzoate,
 10 tetramethylammonium trifluoroacetate, and
 tetramethylthiuram disulfide (TMTDS).

36. The method of claim 27 wherein said fluoride source comprises a compound having the formula $R_1R_2R_3R_4NF$ in which each of the R groups is hydrogen atoms or aliphatic, and wherein said metal chelating agent has the formula:

15 X-CHR-Y, in which

R is either hydrogen or an aliphatic group, and

X and Y are functional groups containing multiply-bonded moieties having electron-withdrawing properties.

20 37. The method of claim 27 wherein said fluoride source comprises a compound having the formula $R_1R_2R_3R_4NF$ in which each of the R groups is hydrogen or aliphatic, and wherein said metal chelating agent has the formula, $R_1R_2R_3R_4N^+ \cdot C_2CCF_3$ in which each of the R groups is hydrogen or aliphatic.

38. The method of claim 27, wherein said nitrogen-containing carboxylic acid has the formula:



wherein each of R and R' is independently selected from the group consisting of hydrogen, alkyl, aryl, and carboxylic acid.

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39. A method of removing residue from a wafer following a resist plasma ashing step on said wafer, comprising contacting the wafer with a cleaning formulation, including (i) a fluoride source, (ii) at least one organic amine, (iii) a nitrogen-containing carboxylic acid or an imine, (iv) water, and optionally at least one metal chelating agent.

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40. A wafer cleaning formulation, including (i) a fluoride source, (ii) at least one organic amine, (iii) a nitrogen-containing carboxylic acid or an imine, (iv) water, and optionally at least one metal chelating agent.

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